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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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12/20/02**INVENTOR(S)**

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 Additional inventors are being named on the _____ separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)**

Miniatrized Gas Sensors featuring electrical breakdown in the vicinity of Carbon Nanotube Tips.

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ENCLOSED APPLICATION PARTS (check all that apply) Specification Number of Pages
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 Application Data Sheet. See 37 CFR 1.76**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT** Applicant claims small entity status. See 37 CFR 1.27.FILING FEE
AMOUNT (\$) A check or money order is enclosed to cover the filing fees

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 The Commissioner is hereby authorized to charge filing
fees or credit any overpayment to Deposit Account Number: Payment by credit card. Form PTO-2038 is attached.The invention was made by an agency of the United States Government or under a contract with an agency of the
United States Government. No. Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted

SIGNATURE

TYPED or PRINTED NAME Charles F. RancourtTELEPHONE (518) 276-6023Date 12/20/02REGISTRATION NO.
(if appropriate)
Docket Number:RPI-740**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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Docket Number	RPI-740
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4th October 2002

INVENTION: Miniaturized Gas Sensors Featuring Electrical Breakdown in the Vicinity of Carbon Nanotube Tips

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INVENTION: Miniaturized Gas Sensors Featuring Electrical Breakdown in the Vicinity of Carbon Nanotube Tips

CONVENTIONAL GAS SENSING TECHNIQUES

Sensing gas molecules is critical to environmental monitoring, control of chemical processes, space missions as well as agricultural and medical applications. Existing electrical sensor materials are based on semi-conducting metal oxides¹⁻³, silicon devices⁴⁻⁵, organic materials⁶⁻⁷ and gas responsive polymers or ceramics⁸⁻¹³. To achieve high chemical sensitivity, semi-conducting metal oxide sensors must be operated at elevated temperatures (200 to 600° C) in order to achieve the required chemical reactivity between gas molecules and the sensor material¹. This need for high temperature operation increases the device complexity and renders them unsuitable for real-time environmental monitoring. On the other hand, conducting polymers and organic semi-conductors are suitable for room temperature operation, but exhibit limited sensitivity⁶, and are characterized by very high resistivity (sample resistance >10 giga ohms⁷). Because of these limitations there is a need to develop new "Enabling Materials" for gas sensing that will allow for operation at room temperature and atmospheric pressure and provide for high-sensitivity measurements and low response times.

NANOTUBES AS MINIATURIZED CHEMICAL SENSORS

The electrical conductance of semi-conducting carbon nanotubes changes sensitively at room temperature on exposure to several gases¹⁴⁻¹⁸ due to charge transfer between adsorbed gas molecules and nanotubes. For example singlewalled nanotube (SWNT) samples are found to exhibit large increase in conductivity on exposure to oxygen¹⁴. Similarly hole doped (p-type) semi-conducting nanotubes exhibit three orders of magnitude increase¹⁵⁻¹⁶ in conductance on exposure to 200 ppm of NO₂ with response times of 2-10 seconds. On exposure to 1% NH₃ flow, the same nanotubes exhibited a two orders of magnitude decrease¹⁵⁻¹⁶ in conductance with response time of 1-2 minutes. Since O₂ and NO₂ are strong oxidizing agents, they attract electrons from the p-type SWNTs, thereby increasing the number of conducting holes. This hole (or p-type doping) shifts the Fermi level closer to the valence band causing increase in conductance. On the other hand, reducing agents such as NH₃ that inject electrons into p-type SWNTs reduce the number of holes, leading to reduced conductance (NH₃ interacts with SWNT surface through other species that act as linkers). It should be noted that the ability of gas species to donate or accept electrons from semi-conducting SWNTs is a necessary but not sufficient condition for influencing the nanotube electrical conductivity. The binding of gas molecules to the nanotube surface must also be taken into consideration; gas species that exhibit low adsorption energy¹⁶⁻¹⁷ and poor diffusion kinetics may not be able to affect nanotube conductance.

LIMITATIONS OF SWNT ELECTRICAL CONDUCTIVITY MEASUREMENTS

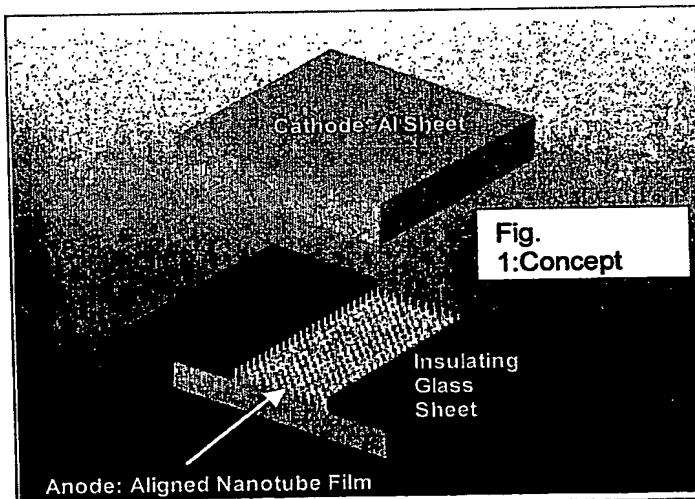
The chemical sensitivity of semi-conducting nanotubes has created considerable interest in the research community regarding the potential application of nanotubes as miniaturized, affordable sensors. However there are many barriers to successful implementation of this technology:

- 1) Nanotubes may not be able to distinguish one chemical or gas from another. For example, exposure to NO₂ causes an increase¹⁵ in nanotube conductance. However as shown in Ref. 14 and 17, a similar increase in conductance could also be generated by exposure to a different oxidizing agent such as O₂.
- 2) It may not be possible to identify gases in a mixture and determine the relative concentrations of the component gases. Since nanotubes are sensitive to so many different types of chemicals, it is possible to combine different gases in different concentrations to yield the same net change in conductance. For example; exposure to 1% NH₃ causes a decrease¹⁵⁻¹⁶ in nanotube conductance of ~ 2×10⁻⁶, while exposure to 2 ppm of NO₂ causes an increase¹⁵⁻¹⁶ in conductance of ~ 2×10⁻⁶. Therefore a mixture that contains 2 ppm of NO₂ and 1% NH₃ may not create any net change in the SWNT conductivity.

- 3) Conductivity measurements cannot be used to identify gas species that are unable to exchange charge with SWNTs. For example an inert gas such as argon (Ar) cannot be identified by nanotubes, since Ar molecules are incapable of either donating or accepting electrons from semi-conducting SWNTs.
- 4) It is not possible to identify gas species that are incapable of being adsorbed by nanotubes. For example first-principles calculations¹⁶ using density functional theory show that semi-conducting SWNTs cannot sense carbon monoxide (CO) due to poor binding. These results are in agreement with experimental observations¹⁶.
- 5) Conductivity changes that occur via physisorption are reversible¹⁵ but require ~ 12 hours for complete recovery at room temperature; this process can be accelerated to ~ 1 hour by heating to 200°C in an inert Ar environment. However, if the adsorption mechanism is dominated by chemisorption (as is the case with certain gases¹⁷ such as NH₃), then this leads to an irreversible change in nanotube electrical conductivity. In such cases, the sensor cannot be used repeatedly and has to be discarded after use.
- 6) It is also well known that the electrical conductivity of SWNTs is exquisitely sensitive to changes in the environmental conditions such as moisture, temperature, residual charge build-up or contamination and this creates additional difficulties for reliable and repeatable sensing.

PROPOSED CONCEPT

We propose a novel concept for gas-sensing that could potentially overcome some of the limitations described in the previous section. The concept proposes a radical departure from conventional nanotube electrical conductivity measurements; we propose to take advantage of the extremely high electric fields that are generated near nanotube tips as a means of inducing electrical breakdown of the gas at low voltages. Fig. 1 shows a schematic of the proposed arc-discharge device. The control voltage is applied between the anode (MWNT film) and cathode (Al sheet). Since the nanotubes within the film are densely packed, inter-tube tunneling effects result in the aggregate MWNT-film behaving like a conducting sheet electrode. Contacts can be established either on the surface of the film or via the substrate (e.g. for films grown on gold). The electric field¹⁹⁻²⁰ in vicinity of the nanotube tips can be represented as; $E=V/R$, where V is the applied voltage and R is the nanotube tip curvature. Our goal is to take advantage of the extremely small tip curvature of nanotubes ($R \sim 15$ nm for MWNTs and $R \sim 0.5$ nm for SWNTs) to create very high non-linear electric fields near nanotube tips. This hastens the breakdown process due to formation of a "corona" or conducting filament of highly ionized gas that surrounds the MWNT tips. This promotes the formation of a powerful electron avalanche or plasma streamer that bridges the gap between the electrodes and allows for a self-sustaining inter-electrode arc discharge to be created at relatively low voltages. Lowering the device voltage is very important for safe operation of the gas sensor. Reduction in the operating voltage can also enable battery-powered operation; which holds the key for compact, affordable nano-electronic sensor development. The novelty in the proposed approach lies in the innovative use of multi-walled carbon nanotube arrays to amplify the electric field near the electrode by imparting a nano-scale curvature to the electrode surface.



The proposed technique is extremely powerful because: 1) By monitoring the voltage at which the breakdown occurs, the gas can be identified; it is well established that at a constant temperature and pressure every gas has a unique²¹⁻²² breakdown electric field, 2) By monitoring the self-sustaining discharge current, the gas concentration can be determined, 3) Since all gases display a characteristic breakdown response, any non-flammable gas (including inert species such as Ar), can be detected, as opposed to conductivity measurements that are limited to gas species that exhibit adsorption and charge transfer with nanotubes, 4) Since this technique does not involve adsorption/desorption of gas species, the sensor displays fast response time and is not limited by considerations of reversibility and 5) This approach can be extended to gas mixtures by limiting the volume of gas affected by the ionization. This ensures that the gas being sensed does not get replenished as molecules breakdown and are ionized, allowing for continued sensing at higher voltages to detect the next gas in the mixture.

DEMONSTRATION OF CONCEPT FEASIBILITY

This section shows the technical feasibility of nanotube arc-discharge sensors.

A) MWNT Electrodes vs. Metal Electrodes

The MWNT film used for this test was developed by the catalytic chemical vapor deposition of xylene-ferrocene mixture precursor²³⁻²⁵ on SiO₂ substrate in Ar atmosphere at 800° C. Individual nanotube dimensions correspond to ~30 nm outer diameter (R=15 nm), ~10 nm of wall thickness, and ~30 μm in length. Center-to-center distance between individual tubes in the films was determined to be ~ 50 nm. The device was tested in air (Fig. 2, 3) with anode-cathode separation of 150 μm. Continuous current discharge of

460 μA was generated at 346 V. Tests were repeated with metal electrodes (no nanotubes were used), while maintaining the electrode separation as 150 μm. For this case breakdown of air occurred at 960 V

with current discharge of 69 μA. These extremely promising results indicate that by the novel use of MWNTs as the anode, the breakdown of air can be reduced from 960 V to 346 V (65% reduction), due to extremely high localized electric fields created near MWNT tips. The discharge current is also increased from 69 μA to 460 μA, (566% increase) leading to high sensitivity. We believe that this is related to the high density of MWNTs that constitute the surface of the electrode. There are literally billions of perfectly aligned tubes that decorate the substrate; such a consistent nano-scale roughness is unprecedented for metal electrodes. Each tip creates a localized plasma of highly ionized gas that extends out from the anode; greatly increasing the net volume of conducting gas and consequently the discharge current.

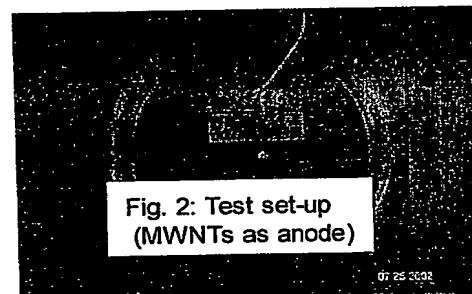


Fig. 2: Test set-up
(MWNTs as anode)

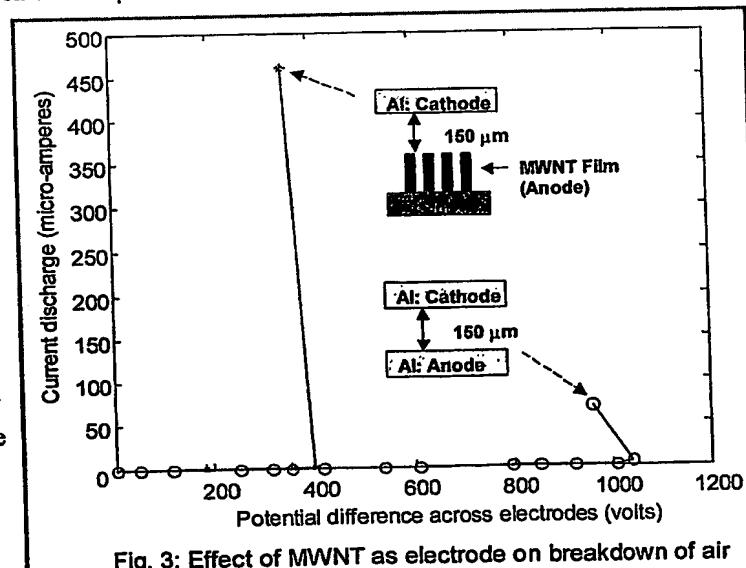


Fig. 3: Effect of MWNT as electrode on breakdown of air

B) Identification of Gas Species

The arc-discharge device with MWNT film as anode was used to detect the identity of several gas species such as helium, argon, nitrogen and air. For all tests shown in this section the anode-cathode separation was maintained as 150 μm .

The nanotube device was placed in an environmental chamber with electrical feed through. First, air was pumped out of the chamber to establish a vacuum (pressure: 10^{-7} Torr). Next, the gas to be identified was released in a controlled fashion. Breakdown data was recorded over a wide range of gas concentrations (10^{-7} to 10^{-1} moles/litre). Fig. 4 shows the breakdown voltages of several gases at room temperature (300° K) and at a chamber pressure of 760 Torr, i.e. gas concentration of 4×10^{-2} moles/litre.

Note that each gas exhibits a distinct breakdown behavior; helium displays the lowest (164 V) and nitrogen shows the highest (390 V) breakdown voltage.

Recent work¹⁹ at the Xi'an Jiaotong University in China using nanotubes anchored in porous silicon (as cathodes)

has also shown that different species exhibit different breakdown voltages at 760 Torr gas pressure. However the effect of gas concentration on the discharge properties has not been addressed so far.

To study this effect we have conducted testing of gas species at reduced pressures (Fig. 5, 6).

Figure 5 shows the effect of concentration on the breakdown voltages of air, Ar and He. No significant change in the breakdown voltage is observed for different concentrations. This is somewhat contrary to Paschen's law for uniform electric field²², which predicts an increase in breakdown voltages at very low and very high values of pressure (the pressure is proportional to concentration for a fixed chamber volume). These results can be explained by the fact that breakdown in this case is strongly affected by highly non-linear electric fields near MWNTs, resulting in a pre-breakdown plasma that helps to bridge the electrode gap and reduces the sensitivity of breakdown voltage to pressure. Our tests with nanotube

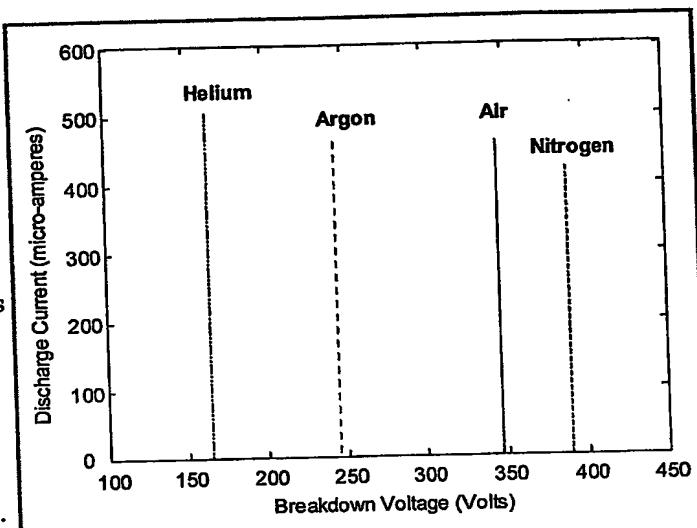


Fig. 4: Breakdown voltages for different gas species

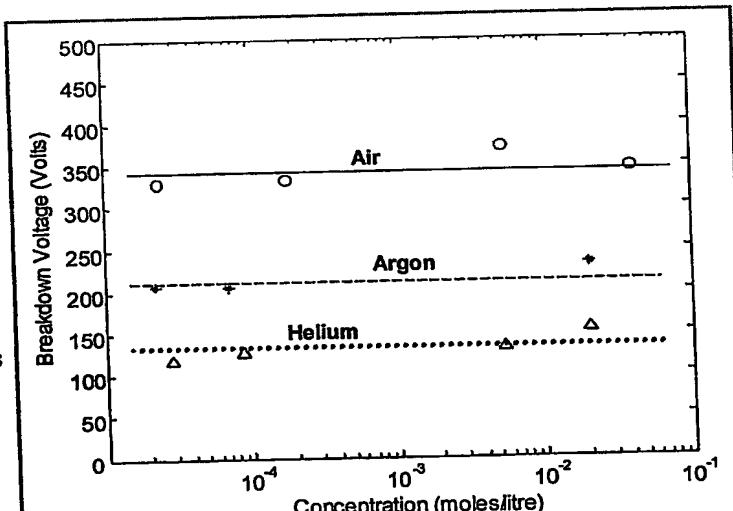


Fig. 5: Effect of gas concentration on breakdown voltage

arc discharge devices indicate that for a fixed inter-electrode spacing, the breakdown voltage of each gas is unique and depends mainly on the electric field and is only weakly affected by concentration of the gas (this is valid over a wide range as shown in Fig. 5). Therefore by simply monitoring the breakdown voltage of the gas, its identity can be established. These results are repeatable and were verified by testing several samples.

C) Gas Concentrations

Having determined the identity of the unknown gas, the next step involves the determination of the gas concentration. Fig. 6 shows the self-sustaining current discharge at breakdown for three different gas species; Ar, N₂ and air. Note that the discharge current varies linearly with gas concentration. This trend is valid over a wide range of gas concentrations ranging from 10⁻⁷ to 10⁻¹ moles/litre. These very encouraging results demonstrate that the self-sustaining arc-discharge current generated at breakdown is a characteristic property of the number of gas molecules per unit volume

that are available for conduction. This implies that by monitoring the self-sustaining discharge current generated at breakdown, the concentration of the unknown gas species can be established.

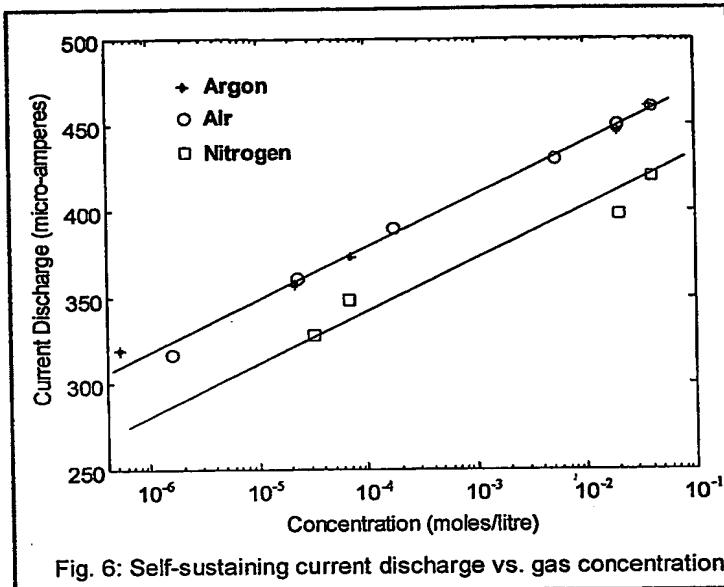


Fig. 6: Self-sustaining current discharge vs. gas concentration

FUTURE DEVELOPMENT

The results shown in the previous section indicate that an arc-discharge device with MWNT film as the electrode can be used to detect the identity of an unknown gas and determine its concentration. However the voltage inputs needed to enable gas breakdown are in the range of 150-350 V. In order to enable battery-powered operation, it becomes necessary to bring the device operating voltages down to below 100 V. To achieve this we propose to use single walled carbon nanotube arc discharge devices.

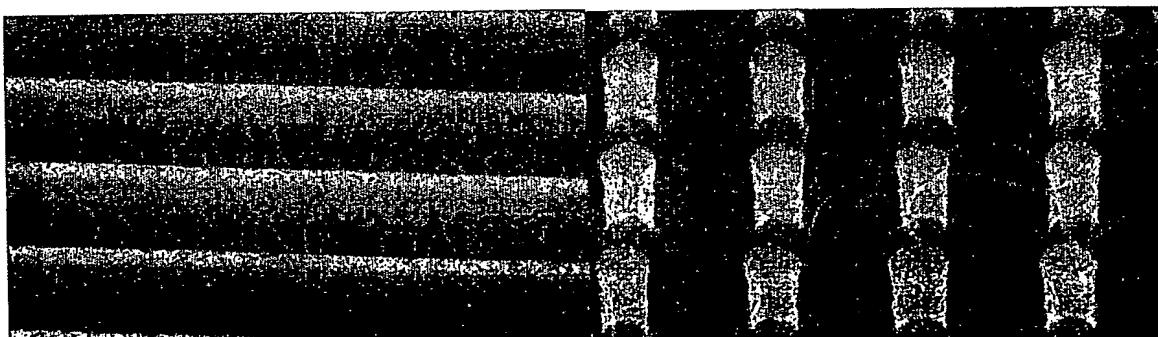


Fig. 7: SWNTs are grown between bridges (left image) or pillars (right image) of Si features on which a thin metal layer is deposited. We envision these bridges as the device electrodes. SWNT density can be varied, by changing the growth parameters. Separation between the bridges can also be varied via the mask used for lithography. The SWNTs can also be straightened, cut and manipulated using the Focused Ion beam (FIB) technique.

Singlewalled nanotubes (SWNTs) have much smaller diameters (1 nm) than MWNTs (30 nm) and because of their smaller dimensions the electric field in the vicinity of SWNT tips is expected to be far greater than MWNTs. Indeed in a related study²⁶ we have recently found that at a particular applied voltage, the electric field of carbon nanotube of similar length depends critically on the curvature of the nanotube, with over 30 times field enhancement predicted for SWNTs compared to MWNTs.

Design of an SWNT based arc-discharge device is challenging because so far it has not been possible to grow vertically oriented SWNTs on any type of substrate. On the other hand, horizontal networks of SWNTs can be grown between pre-patterned, metal deposited locations on Si substrate. We have made excellent progress in this, as can be observed in a typical image (Fig. 7) showing the growth of SWNTs. We envisage that once these networks are grown, they could be cut using a focused ion beam (FIB) to expose the cut, free ends of separated SWNT. When a voltage is applied across the electrodes (metal coated silicon features, Fig. 7), the broken ends (tips) would be connected by highly non-linear electric lines of force that could significantly reduce the breakdown voltages.

To detect flammable gases we propose to develop an ionization micro-chamber (Fig. 8a) into which we inject, isolate and test a very small quantity of the mixture. All flammable species require a certain minimum concentration threshold of oxygen without which combustion cannot occur and the required oxygen concentration may not be available in the micro-chamber. Even if the flammable specie ignites the control volume is limited to a very small test sample and this eliminates any safety concerns associated with testing of the flammable specie. There are also several reasons why the ionization micro-chamber will improve sensor performance: 1) testing a small volume of gas improves fidelity and repeatability of results, 2) due to smaller control volume, the settling time and mixture diffusivity is better, and 3) the ionization micro-chamber lends itself to system miniaturization; we envision a device the size of a chip that includes the micro-chamber coupled to a controller that performs the impulse voltage scan and continuously monitors the current discharge responses.

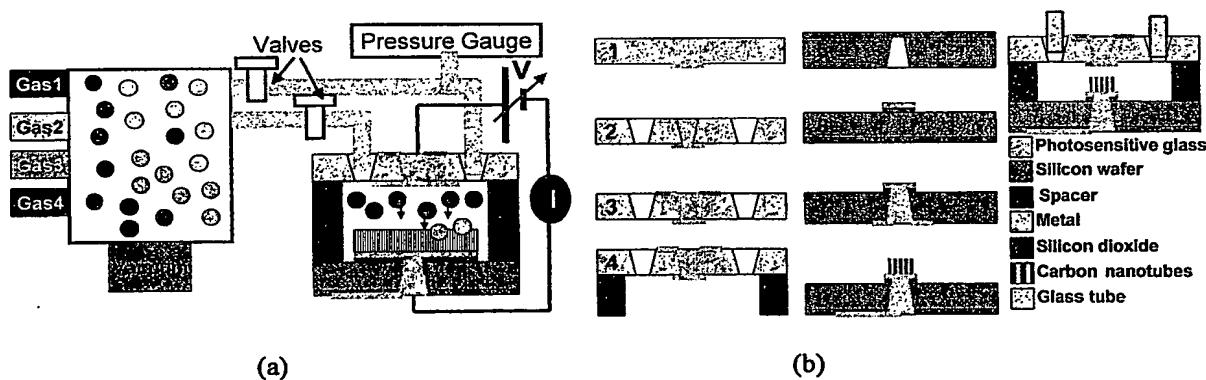


Figure 8. (a) Schematic of proposed ionization microchamber system and (b) Major fabrication steps for a CNT-silicon-glass-microchamber.

Custom microfabrication allows for flexibility in design, while miniaturization offers the opportunity to develop small-volume chambers (e.g. 25 nanoliters for a $500 \mu\text{m} \times 500 \mu\text{m} \times 100 \mu\text{m}$ chamber) with fast response time. Several designs with different chamber size, electrode size, electrode material and inter-electrode distance will be fabricated and tested. For the design shown in Fig. 8b, the top-side of the device carries the metal electrode and the gas inlet/outlet ports, while the bottom-side carries the nanotube electrode; inter-electrode gap is controlled by a spacer. The sides of the device are fabricated separately on two wafers that are bonded at the end. The MEMS microfabrication steps 1 to 8 (shown in Fig. 8b) employed to fabricate the CNT-silicon-glass-microchamber are:

1) Deposition (e.g. by electron beam evaporation) and patterning (e.g. by wet etching with a photoresist mask) of the metallic electrode on photosensitive glass substrate, 2) Patterning of the photosensitive glass (UV exposure, heat treatment and HF etch) to define the gas inlet/outlet ports and the via-trench for the top electrode. Metal electro-deposition will be used to partially fill the via-trench, 3) Patterning (by lift-off) of the metallic contact pads and contact lines for the top electrode, 4) Deposition and patterning of the spacer (e.g. SU-8 or AZ-4000 photoresist can be spin-coated at the desired thickness and patterned using UV lithography). Alternatively this step can be skipped if a recess is etched in the glass substrate before step 1, the recess acts as a spacer for desired inter-electrode distance, 5) Deposition (e.g. by Low Pressure Chemical Vapor Deposition) and patterning (e.g. by Reactive Ion etching) of a thick (e.g. ~2 μm) SiO_2 film, and patterning of the via trench (KOH etching) for the CNT electrode, 6) Deposition and patterning (e.g. by lift-off) of the metal film (gold) which serve as seed layer for the selective CNT growth, 7) Partial etching (HF-one side) of the SiO_2 layer underneath the metal film, in order to expose the film and to perform electrodeposition of metal to partially fill the via-trench. Next, metallic contact pads and contact lines are patterned for the CNT electrode, 8) selective deposition of nanotube film (we have shown nanotube patterning on Au substrates in our lab). In the final stage, the two sides are bonded together, and gas tubing is sealed to the gas ports. Bonding techniques include adhesive bonding or anodic bonding depending on the approach used to make the spacer. After wafer bonding, the micro-chamber will be wire bonded to a custom made carrier package which allows access of inlet and outlet gas tubing to the gas ports and electric access to the backside CNT electrode pads. We will adapt existing chip-carriers for these purposes. The micro-chamber will be tested for gas permeability before performing breakdown tests; polymer lid seal, or die coats will be employed if necessary to improve seal of the chambers.

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